

Computational Materials Physics

Project Team 3

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Abstract

Density functional theory was used to study the stability of Te_2O_5 crystal structure and five Te-O-H molecules with an oxygen tetrahedron and the tellurium atom in the center. The stability of these molecules was studied by calculating their formation energies. The results show that at least HTeO_4 , H_2TeO_4 and H_4TeO_4 are stable. H_3TeO_4 had the largest formation energy but this might be due to inaccurate structure of the molecule.

1 Introduction

Density functional theory (DFT) is the standard tool of describing material at the quantum level and predicting various properties of systems in biology, chemistry and materials science. There are many different DFT codes available, each with their own advantages. In this work, FHI-aims was used [1, 2, 3]. It is an all-electron code utilizing numeric atom-centered basis functions for its electronic structure calculations.

In this project, DFT is used to study the stability of possible new Te-O-H molecules. More specifically, the inspected molecules contain an oxygen tetrahedron, a tellurium at the centroid and additionally 0 to 4 hydrogen atoms. In the larger picture, the molecules of interest are new, unknown Po-containing molecules but polonium is a highly radioactive element meaning experimental research is difficult. It is also a heavier atom than tellurium making it computationally more expensive as relativistic effects have to be accounted for.

2 Numerical convergence

To ensure accurate computational results, sufficient settings for the DFT calculations must first be defined. In FHI-aims, the often used convergence criterion is total energy as evaluation of hydrostatic pressure is not available unlike in e.g. Quantum Espresso. The convergence tests are conducted with respect to both k-grid density and basis set size. Calculating convergence w.r.t. k-grid density is straightforward but since total energy is dependent on the basis set size, the convergence criterion must be changed to the difference in total energy when the volume of the unit cell is slightly altered. That is, the total energy was calculated on the initial crystal [4] and on a second crystal with approximately 2% larger unit cell volume, and the difference in total energy was monitored.

For the k-grid tests, densities 1, 3, 5, 7, and 9 (e.g. $3 \times 3 \times 3$) were used and the figure and table showing the total energies are shown below in Fig. 1 and Tab. 1.

Mesh	Total energy (eV)
$1 \times 1 \times 1$	-770856.972132826
$3 \times 3 \times 3$	-770856.386275078
$5 \times 5 \times 5$	-770856.390952544
$7 \times 7 \times 7$	-770856.390983028
$9 \times 9 \times 9$	-770856.390983915

Table 1: K-grid convergence test table.

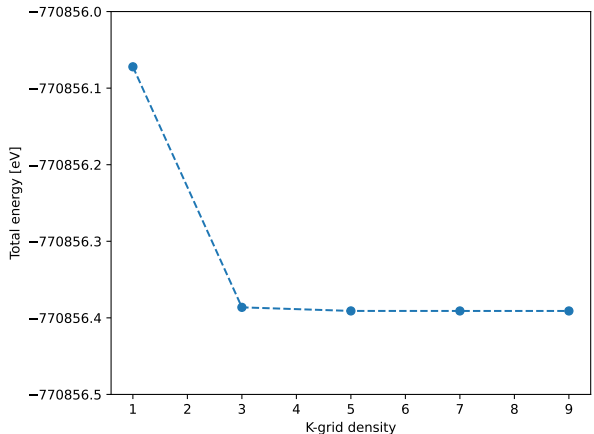


Figure 1: K-grid convergence test plot.

The results show that for a $3 \times 3 \times 3$ -grid, the density is only 4.6 meV larger than for a $5 \times 5 \times 5$ -grid and the system can be considered as converged.

For the basis set, the total energy difference between the original system and a slightly larger system (approx. 2% larger) was monitored. All available basis sets in FHI-aims were tested, more specifically light, intermediate, tight and really tight basis sets. The figure (Fig. 2) and table (Tab. 2) below show the energy difference convergence.

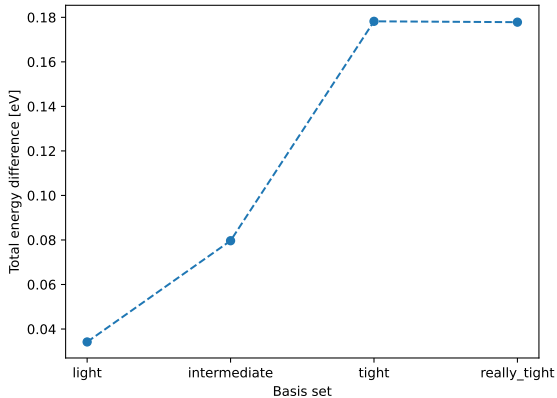


Figure 2: Basis set convergence test plot.

Using the really tight basis changes the energy difference by approximately 0.4 meV and the calculation is considered to have converged.

Basis set	Energy difference (eV)
Light	0.03419
Intermediate	0.07965
Tight	0.17821
Really tight	0.17782

Table 2: Basis set convergence test table.

Figure 3

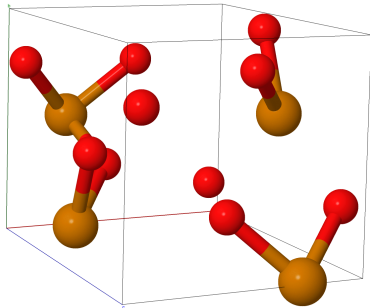


Figure 3: Geometry of the optimized unit cell of the crystal.

3 Geometry optimization and formation energy

Next, the crystal structure of Te_2O_5 was optimized using the converged settings ($3 \times 3 \times 3$ mesh and the tight basis set). The standard geometry optimization technique in FHI-aims is to first run an initial optimization using the light basis set and a subsequent calculation using the tight basis set. This method was also used here. The optimized crystal structure is shown in Fig. 3.

In addition to the geometry optimization, the task was to compute the formation energy of this crystal. It is calculated as the difference of total energy of the crystal and total energy of equal amounts of bulk components. The energy of isolated oxygen is calculated from the O_2 molecule and tellurium is assumed to be in a trigonal ($P3_121$) crystal structure [5]. Numerical convergence for the free molecule calculation was assured by increasing the potential confinement radius in a way suggested in the FHI-aims manual book. The total energy of the crystal and its free components are shown in Tab. 3. The energy for the O_2 molecule was calculated using the optimized distance between the two atoms (126 pm). As the unit cell consists of 4 tellurium and 10 oxygen atoms, the

Input	Total energy (eV)
$2 [\text{Te}_2\text{O}_5]$	$-0.770\,858\,765 \times 10^6$
O_2	$-0.409\,228\,151 \times 10^4$
H_2	$-0.317\,487\,125 \times 10^2$
Te_{P3_121}	$-0.187\,595\,272 \times 10^6$

Table 3: Total energy of the crystal and its components. Calculated with FHI-aims

formation energy per formula unit is calculated

$$E_{\text{form}} = E_{\text{crystal}} - E_{\text{atoms}} \quad (1)$$

$$= E_{2[\text{Te}_2\text{O}_5]} - 5E_{\text{O}_2} + \frac{4}{3}E_{\text{Te}} \quad (2)$$

$$= -16.266\,466\,891 \text{ eV}, \quad (3)$$

where the energy of tellurium is divided by three since the primitive unit cell of the Te crystal consists of three atoms. Considering the unit cell contains of 14 atoms, the formation energy per atom is -1.162 eV which is somewhat smaller than the given value -1.429 eV . There are at least two possible sources where the difference might have come from: 1) Materials Project computes formation energy in a different way or 2) the obtained results are incorrect. A third option was that Materials Project calculates formation energy using the unrelaxed crystal and its total energy is significantly different. However, the total energy calculation was replicated for the unrelaxed crystal and this did not resolve the discrepancy.

4 Molecular calculations – new Te-O-H molecules

Since FHI-aims supports non-periodic calculations intrinsically, there is no need for supercell calculations and we could consider the free-standing molecule directly. The task was to study the stability of molecules with a tellurium atom at the center of an oxygen tetrahedron and 0 to 4 hydrogen atoms included. That is, we optimized the geometries and calculated the formation energies ($E[\text{TeO}_4] \dots E[\text{H}_4\text{TeO}_4]$). Except for TeO_4 , these are all tellurium oxoacids. As an initial guess for the atomic positions, orthosilicic acid H_4SiO_4 was used as a template since it is a tetrahedron-shaped molecule with Si at the center. The Te-O-H molecules with less than 4 hydrogen atoms were created by removing a suitable number of hydrogens.

The optimized geometries of all considered molecules and the template molecule are presented in Fig. 4. The three smallest molecules TeO_4 , HTeO_4 and H_2TeO_4 all retain their tetrahedron shape. The larger molecules

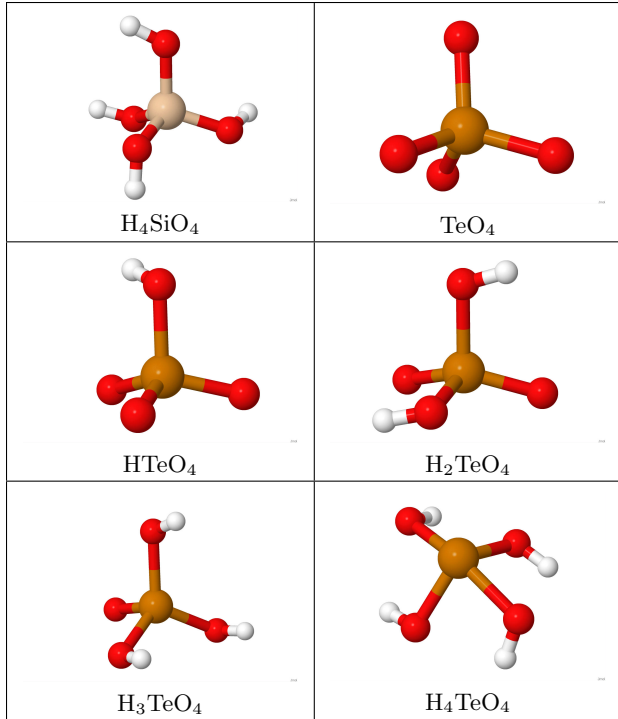


Figure 4: Optimized geometries of all 5 H_xTeO_4 molecules and the template molecule H_4SiO_4 .

Molecule	Total energy [eV]	E_{form} [eV]
TeO_4	$-0.195\,779\,670\,911 \times 10^6$	0.164
$HTeO_4$	$-0.195\,798\,712\,312 \times 10^6$	-3.002
H_2TeO_4	$-0.195\,817\,680\,723 \times 10^6$	-6.097
H_3TeO_4	$-0.195\,833\,967\,869 \times 10^6$	-22.384
H_4TeO_4	$-0.195\,853\,067\,028 \times 10^6$	-9.735

Table 4: Total and formation energies of studied molecules.

H_3TeO_4 and H_4TeO_4 however lose the original shape. For the H_3 variant the tetrahedron is lost in a way that brings the tellurium atom and the oxygen atoms of the hydroxy groups almost into the same plane. The molecule with four hydrogen atoms completely loses its original shape and all oxygen atoms are located on the same side w.r.t. the center. While the last molecule at a first glance looks very different compared to the other molecules, there are examples of similar structures in literature (e.g. orthocarbonic acid). Also, at an intuitive level the structure makes sense as the hydrogen atoms want to form hydrogen bonds with oxygen atoms.

To reveal more information of the stability of these molecules, the formation energy of each one has to be inspected. It is calculated by comparing the total energy of the molecule to the energy of equal amount

of free oxygen and hydrogen molecules or bulk tellurium which was again considered to be in a trigonal unit cell. The calculated formation energies per molecule are presented in Tab. 4. The molecules with 1 or more hydrogen atoms show negative formation energy suggesting they are stable while TeO_4 has a very slight positive formation energy.

Combining the unusual geometry and very negative formation energy of H_3TeO_4 could however mean that the DFT calculation did not provide accurate results in that case. This would be further supported by the fact that tellurium only appears in oxidation states -II, +IV or +VI in acids containing oxygen, hydrogen and tellurium [6]. The most common oxidation state for oxygen is -II and for hydrogen it is +I which would result in a non-zero oxidation number for the acid which is not common.

The formation energies of $HTeO_4$, H_2TeO_4 and H_4TeO_4 suggest that these molecules would be stable. For the latter molecules this is supported by looking at the total oxidation numbers which are zero, and the tellurium atom has the oxidation numbers of +IV and +VI in these molecules, respectively.

5 Conclusions

We studied Te-O-H molecules in which the tellurium atom is in the center of an oxygen tetrahedron with 0 to 4 hydrogen atoms. The FHI-aims code was used to optimize the geometries and to calculate the formation energies thus giving us a look into the stability of these inspected molecules. FHI-aims supports free molecule calculations directly which means no supercells were needed. Numerical convergence was assured by using the tight basis set for all molecules. Optimizing for the k-grid density was not necessary since the free molecule calculations were not periodic.

Of the inspected molecules, all but TeO_4 had negative formation energy suggesting stability but the unusual geometry and the very large negative formation energy of H_3TeO_4 raised doubts on the accuracy of the calculation on that case. H_2TeO_4 and H_4TeO_4 seemed to be very stable and this was supported by the oxidation numbers of the elements. $HTeO_4$ also had a negative formation energy, and looking at oxidation numbers would suggest that it would be a negative ion with a charge of -1.

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